Metallic charge density waves and surface Mott insulators for adlayer structures on semiconductors: extended Hubbard modeling

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Motivated by the recent experimental evidence of commensurate surface CDW in Pb/Ge(111) and Sn/Ge(111) $\sqrt{3}$-adlayer structures, as well as by the insulating states found on K/Si(111):B and SiC(0001), we have investigated the role of electron-electron interactions, and also of electron-phonon coupling, on the narrow surface state band originating from the dangling bond orbitals of the adsorbate. We model the problem by an extended two-dimensional Hubbard model at half-filling on a triangular lattice. We include an on-site Hubbard repulsion U and a nearest-neighbor V, plus a long-ranged Coulomb tail. The electron-phonon interaction is treated in the deformation potential approximation. We have explored the phase diagram of the model including the possibility of commensurate 3×3 phases, using mainly the Hartree-Fock approximation. For U larger than the bandwidth we find magnetic insulators, possibly corresponding to the situation in SiC and in K/Si. For smaller U, the inter-site repulsion V can stabilize metallic CDW phases, reminiscent of the 3×3 structures of Sn/Ge, and possibly of Pb/Ge.

I. INTRODUCTION

Pb and Sn $\sqrt{3}$-adlayer structures on the (111) surface of Ge have recently revealed a charge density wave (CDW) instability to a low temperature reconstructed 3×3 phase. [1,2,4,5,3] The low temperature phase is either metallic – as seems to be the case for Sn/Ge(111) – or weakly gapped, or pseudo-gapped, as suggested for Pb/Ge(111). Related systems, like the $\sqrt{3}$-adlayer of Si on the (0001) surface of SiC [6] and on K/Si(111):B, [7] show, instead, a clear insulating behavior – with a large gap – with no structural anomalies or CDWs investigated so far. Two-dimensional Fermi surface (FS) nesting in the half-filled surface states [8] has been invoked as the driving mechanism for the CDW instability in the case of Pb/Ge, [1] but excluded for the case of Sn/Ge. [3]

As all these systems appear to belong together in the same class, we should begin with a discussion that in principle encompasses all of them. We believe the following points to be of general validity: *i)* **Poor nesting**. An unbiased interpretation of the photoemission experiments, [2,4,5] and a close examination of the existing local density approximation (LDA) calculations [1,9,3] of the surface ("adatom dangling bond") half-filled band do not indicate good nesting of the FS at the surface Brillouin zone (BZ) corner $\mathbf{K} = (4\pi/3a, 0)$. We believe this to be equally true for Pb/Ge as for Sn/Ge, contrary to what stated in the literature. [1] Fig. 1, showing the LDA surface band dispersion for the test-case of Si(111)/Si, [9] as well as the corresponding FS and Lindhard density response function, provides a concrete illustration of these statements. *ii)* **Importance of electron-electron interactions**. The width W of the surface band is relatively small ($W \approx 0.5$ eV for Pb-Sn/Ge, ≈ 0.3 eV for SiC). Moreover, this band is half-filled. These facts call for a careful consideration of electron-electron interactions, and not just electron-phonon (e-ph), as a possible source of instability. This is reinforced by noting the different phenomenology of SiC and K/Si:B with respect to Pb-Sn/Ge, the stronger insulating character of the former paralleling closely their stronger electron-electron repulsions, connected with larger bulk semiconducting gaps. *iii)* **Weakness of LDA**. LDA is certainly suitable for calculating

realistic bands in a weakly interacting system, but is less reliable, at least without including spin, in predicting the instabilities of a narrow band. For instance, the phenomenology of SiC(0001) – suggesting a Mott-Hubbard insulator – is unreproducible by LDA. The very onset of a CDW on Sn/Ge(111) does not seem to be predicted by recent LDA calculations. [3] *iv)* **Different mechanisms for 3×3 CDW instabilities**. There are at least two different mechanisms which can influence the CDW formation: a) on-site, and nearest-neighbor (n.n.) electron-electron repulsion b) on-site effective attraction (negative Hubbard-U term) of e-ph origin. Of these, the n.n. repulsion naturally suggests, as we shall see, the 3×3 surface periodicity, which is found experimentally. Electron-phonon alone would not in itself appear to drive a 3×3 CDW. At weak coupling, the band structure dominates and incommensurate structures could be preferred. At strong coupling, the frustration associated to the triangular lattice, will favor, in general, a superconducting ground state over a CDW phase. [10].

The approach we take here is based on an extended Hubbard-Holstein model. It is by necessity a "non-first-principle" approach and, as such, it has no strong predictive power. We have found it very helpful, however, in clarifying the possible scenarios as a function of physical parameters.

II. MODEL

The basic starting point is the half-filled surface state band $\epsilon_{\mathbf{k}}$ which one calculates in LDA, and is found to lie in the bulk gap. [1,9] We write our effective Hamiltonian as follows:

$$H = \sum_{\mathbf{k}}^{BZ}\sum_{\sigma}\epsilon_{\mathbf{k}}c^{\dagger}_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + H_{\rm ph} + H_{\rm e-ph} + H_{\rm int}\ , \tag{1}$$

where $c^{\dagger}_{\mathbf{k},\sigma}$ is the Bloch surface state, whose Wannier function is centered on the adatom, as can be seen in Ref. [9]. $H_{\rm int}$ includes correlation effects which are not correctly accounted for within LDA, which we parametrize as follows:

$$H_{\rm int} = U\sum_{\mathbf{r}} n_{\mathbf{r},\uparrow}n_{\mathbf{r},\downarrow} + \frac{1}{2}\sum_{\mathbf{r}\neq\mathbf{r}'} V_{\mathbf{r}-\mathbf{r}'}(n_{\mathbf{r}}-1)(n_{\mathbf{r}'}-1)\ . \tag{2}$$

Here U is an effective repulsion (Hubbard-U) for two electrons on the same adatom Wannier orbital, and $V_{\mathbf{r}-\mathbf{r}'}$ is the direct Coulomb interaction between different sites $\mathbf{r}$ and $\mathbf{r}'$. We have considered two models for $V_{\mathbf{r}-\mathbf{r}'}$: 1) a truncation to a n.n. V, and 2) a model with a Coulomb tail $V_{\mathbf{r}-\mathbf{r}'} = Va/|\mathbf{r}-\mathbf{r}'|$. The results for case 2) are qualitatively similar to those of 1), and will be discussed elsewhere. [11] LDA estimates of the bare repulsions U_o and V_o between two electrons on the same and on neighboring Wannier orbitals are – for our test case of Si(111)/Si – of about 3.6 eV and 1.8 eV respectively. [9] Screening effects by the the underlying bulk are expected to reduce very substantially these repulsive energies. A conservative lower bound for U and V is obtained dividing their bare values by the image-charge screening factor, $(\epsilon+1)/2 \approx 6$, yielding $U = 0.6$ eV, and $V = 0.3$ eV. As for the e-ph interaction, in principle both the on-site Wannier state energy and the hopping matrix elements between first neighbors depend on the positions of the adatoms. Within the deformation potential approximation, we consider only a linear dependence of the on-site energy from a single ionic coordinate (for instance, the height $z_{\mathbf{r}}$ of the adatom measured from the equilibrium position), and take $H_{\rm e-ph} = -g\sum_{\mathbf{r}} z_{\mathbf{r}}(n_{\mathbf{r}}-1)$. The free-phonon term will have the usual form $H_{\rm ph} = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \left(b^{\dagger}_{\mathbf{k}} b_{\mathbf{k}} + 1/2\right)$, where $b_{\mathbf{k}}$ is the phonon annihilation operator. An order-of-magnitude estimate for g is ≈ 1 eV/$\mathring{A}$.

III. PHASE DIAGRAM.

We consider first the purely electronic problem in the absence of e-ph interaction. We start the discussion from particular limiting cases for which exact statements, or at least well-controlled ones, can be made.

Large positive U: the Mott insulator. For $U \gg V, W$, the system is deep inside the Mott insulating regime. [12] Within the large manifold of spin degenerate states with exactly one electron per site, the kinetic energy generates, in second order perturbation theory, the Heisenberg spin-1/2 antiferromagnet as the effective Hamiltonian governing the *spin* degrees of freedom, $H_{\rm eff} = \sum_{(ij)} J_{ij} \mathbf{S}_{\mathbf{r}_i} \cdot \mathbf{S}_{\mathbf{r}_j}$, with $J_{ij} = 4|t_{ij}|^2/U$. [12] For our test case of Si(111)/Si,

the values of the hoppings are such that $J_2/J_1 \approx 0.12$ while the remaining couplings $J_3, \cdots$ are very small. Antiferromagnetism is frustrated on the triangular lattice. Zero temperature long range order (LRO) of the three-sublattice 120^o-Néel type – a commensurate spiral spin density wave (s-SDW) – is nevertheless likely to occur for the spin 1/2 antiferromagnetic Heisenberg model with n.n. coupling J_1, and for small enough J_2. In summary, we expect for large values of U a wide-gap Mott insulator with a s-SDW (spins lying in a plane, forming 120^o angles), and a 3×3 *magnetic* unit cell. This is, most likely, the state to be found on the Si-terminated SiC(0001) surface at T=0.

Strong inter-site repulsion: an asymmetric CDW with three inequivalent sites. The e-ph coupling can effectively reduce U, but not V. Therefore, it is of interest to consider the hypothetical regime $W < U \ll V$. In order to minimize the interaction energy, the system will prefer a 3×3 CDW with two electrons on one sublattice (A), a single electron on another sublattice (B), and zero electrons on the third sublattice (C). (See Fig. 2.) The spin degeneracy associated with the (unpaired) electron on sublattice B can be removed, owing to t_2, which leads to an effective spin-1/2 Heisenberg Hamiltonian within sublattice B, with a weak antiferromagnetic exchange constant $J = 4t_2^2/U$. [11]. Summarizing, we expect in this regime a strong 3×3 asymmetric CDW with three inequivalent sites (a-CDW), and a spiral $3\sqrt{3} \times 3\sqrt{3}$ SDW, governing the unpaired electron spins, superimposed on it. This a-CDW is not compatible with the experimental findings on Pb-Sn/Ge, but it could be realized in some other case.

Mean-field theory. In order to get an idea of any additional phases for smaller U, and of the possible phase diagram of the model we turn to a mean field analysis. The first issue is the possibility of magnetism. For small values of the interactions U and V, the Stoner criterion can be used to study the instability of the paramagnetic metal obtained from LDA calculations. The charge and spin susceptibility are given, within the random phase approximation, by $\chi_C(\mathbf{q}) = 2\chi_o(\mathbf{q})/[1 + (U + 2V_\mathbf{q})\chi_o(\mathbf{q})]$, and $\chi_S(\mathbf{q}) = \chi_o(\mathbf{q})/[1 - U\chi_o(\mathbf{q})]$, where χ_o is the non-interacting susceptibility. The divergence of χ_S is governed, in this approximation, by U only. Since $\chi_o(\mathbf{q})$ is finite everywhere, a finite U is needed in order

to destabilize the paramagnetic metal. The wavevector $\mathbf{q}^*$ at which χ_S first diverges, by increasing U, is in general incommensurate with the underlying unit cell. The instability is towards an incommensurate metallic spiral SDW. [13] As for the charge susceptibility, a divergence can be caused only by an attractive Fourier component of the potential $V_{\mathbf{q}}$. $V_{\mathbf{q}}$ has a minimum at the BZ corners $\pm\mathbf{K}$, with $V_{\pm\mathbf{K}} = -3V$. ($V_{\pm\mathbf{K}} \approx -1.54V$ if a Coulomb tail is added). This minimum leads to an instability towards a 3×3 CDW as $(U+2V_{\mathbf{K}})\chi_o(\mathbf{K}) = -1$.

In general, the small coupling paramagnetic metal is surrounded by an intermediate coupling region, where complicated incommensurate – generally metallic – solutions occur. For stronger U and V, commensurate solutions are privileged. [13] In view of the fact that a 3×3 CDW is experimentally relevant, we concentrate our analysis on the simplest commensurate phases. These are easy to study with a standard Hartree-Fock (HF) mean-field theory. [11] In particular, we restrict ourselves to order parameters associated with momentum space averages of the type $\langle c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma'}\rangle$ and $\langle c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k}\pm\mathbf{K},\sigma'}\rangle$, i.e., the uniform magnetization density $\mathbf{m}$, the $\mathbf{K}$-component of the charge density $\rho_{\mathbf{K}} = (1/N)\sum_{\mathbf{k},\sigma}\langle c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k}-\mathbf{K},\sigma}\rangle$, and the $\mathbf{K}$-component of the spin density $\mathbf{S}_{\mathbf{K}} = (1/2N)\sum_{\mathbf{k}}\sum_{\alpha,\beta}\langle c^\dagger_{\mathbf{k},\alpha}(\vec{\sigma})_{\alpha\beta} c_{\mathbf{k}-\mathbf{K},\beta}\rangle$. $\rho_{\mathbf{K}}$ and $\mathbf{S}_{\mathbf{K}}$ have phase freedom, and are generally complex: $\rho_{\mathbf{K}} = |\rho_{\mathbf{K}}|e^{i\phi_\rho}$, etc. The role of the phase is clarified by looking at the real-space distribution within the 3×3 unit cell. For the charge, for instance, $\langle n_{\mathbf{r}_j}\rangle = 1 + 2|\rho_{\mathbf{K}}|\cos(2\pi p_j/3 + \phi_\rho)$, where $p_j = 0, 1, 2$, respectively, on sublattice A, B, and C. The e-ph coupling is included but, after linearization, the displacement order parameter is not independent, and is given by $\langle z_{\mathbf{K}}\rangle = (g/M\omega^2_{\mathbf{K}})\rho_{\mathbf{K}}$. Only the phonon modes at $\pm\mathbf{K}$ couple directly to the CDW. The phonon part of the Hamiltonian can be diagonalized by displacing the oscillators at $\pm\mathbf{K}$. This gives just an extra term in the electronic HF Hamiltonian of the form $\Delta U(\rho^*_{\mathbf{K}}\hat{\rho}_{\mathbf{K}} + \text{H.c.})$, with an energy $\Delta U = -g^2/M\omega^2_{\mathbf{K}}$ which is the relevant coupling parameter. This term acts, effectively, as a negative-U contribution acting only on the charge part of the electronic Hamiltonian.

The mean-field solutions must be compatible with the symmetry of the problem. A symmetry analysis of the Landau theory [14] built from the order parameters $\mathbf{m}$, $\rho_{\mathbf{K}}$, and $\mathbf{S}_{\mathbf{K}}$ shows that: [11] *i*) A CDW can occur without concomitant magnetism. *ii*) A SDW can

occur without a CDW only in the form of a 120^o spiral SDW. In all other cases, a SDW *implies* also a CDW. *iii*) The simultaneous presence of a SDW and a CDW implies, generally, a finite magnetization $\mathbf{m}$, unless the phases of ρ and S are such that $2\phi_\rho + \phi_\sigma = \pi/2 + n\pi$.

We present a brief summary of the mean-field HF calculations for arbitrary U, V, and g. The main phases present in the HF phase diagram are shown in Fig. 2 for the case of $g = 0$. (The diagram is qualitatively similar for $g \neq 0$.) The s-SDW dominates the large U, small V part of the phase diagram, as expected from the Heisenberg model mapping at $U \to \infty$. This is the Mott insulator phase, probably relevant for SiC. Its HF bands are shown in Fig. 3(a). There is however another solution of the HF equations in the large U, small V region. It is an insulating state characterized by a linear z-SDW plus a small CDW with $\phi_\rho = 0$, accompanied by a magnetization $m^z = 1/3$. It lies above the s-SDW by only a small energy difference (of order t_1 per site), and it could be stabilized by other factors (e.g., spin-orbit). A recent LSDA calculation for $\sqrt{3}$-Si/Si(111) has indicated this z-SDW as the ground state, at least if spins are forced to be collinear. [9] The HF bands for this solution are shown in Fig. 3(b). By increasing V, the energies of the s-SDW and of the z-SDW tend to approach, until they cross at a critical value V_c of V. We find $V_c/t_1 \approx 3.3$ at $U/t_1 = 10$. As $V > V_c$, however, the insulating a-CDW prevails. For small values of U and V, or for large enough e-ph coupling g, a *metallic* CDW with $\phi_\rho = 0$ (m-CDW) is found. This may be relevant for the case of Pb and of Sn/Ge(111). (See Fig. 3(c) for the HF bands.) The degree of metallicity of this phase is much reduced relative to the undistorted surface (pseudo-gap). We note that the e-ph interaction can stabilize the $\phi_\rho = 0$ m-CDW also at relatively large U, by countering U with a large negative ΔU. With $g = 1$ eV/$\mathring{A}$, $M_{Si} = 28$, and $\omega_{\mathbf{K}} \approx 30$ meV we get $\Delta U \approx -3t_1$, sufficient to switch from a s-SDW ground state to a m-CDW for, say, $U/t_1 = 8$ and $V/t_1 = 2$. Much larger g's would eventually stabilize a superconducting ground state. [11]

In conclusion, we have found within a single phase diagram three phases, the s-SDW, the z-SDW, and the m-CDW, which may be relevant, respectively, to SiC(0001), to K/Si(111):B, and to Pb or Sn/Ge(111).

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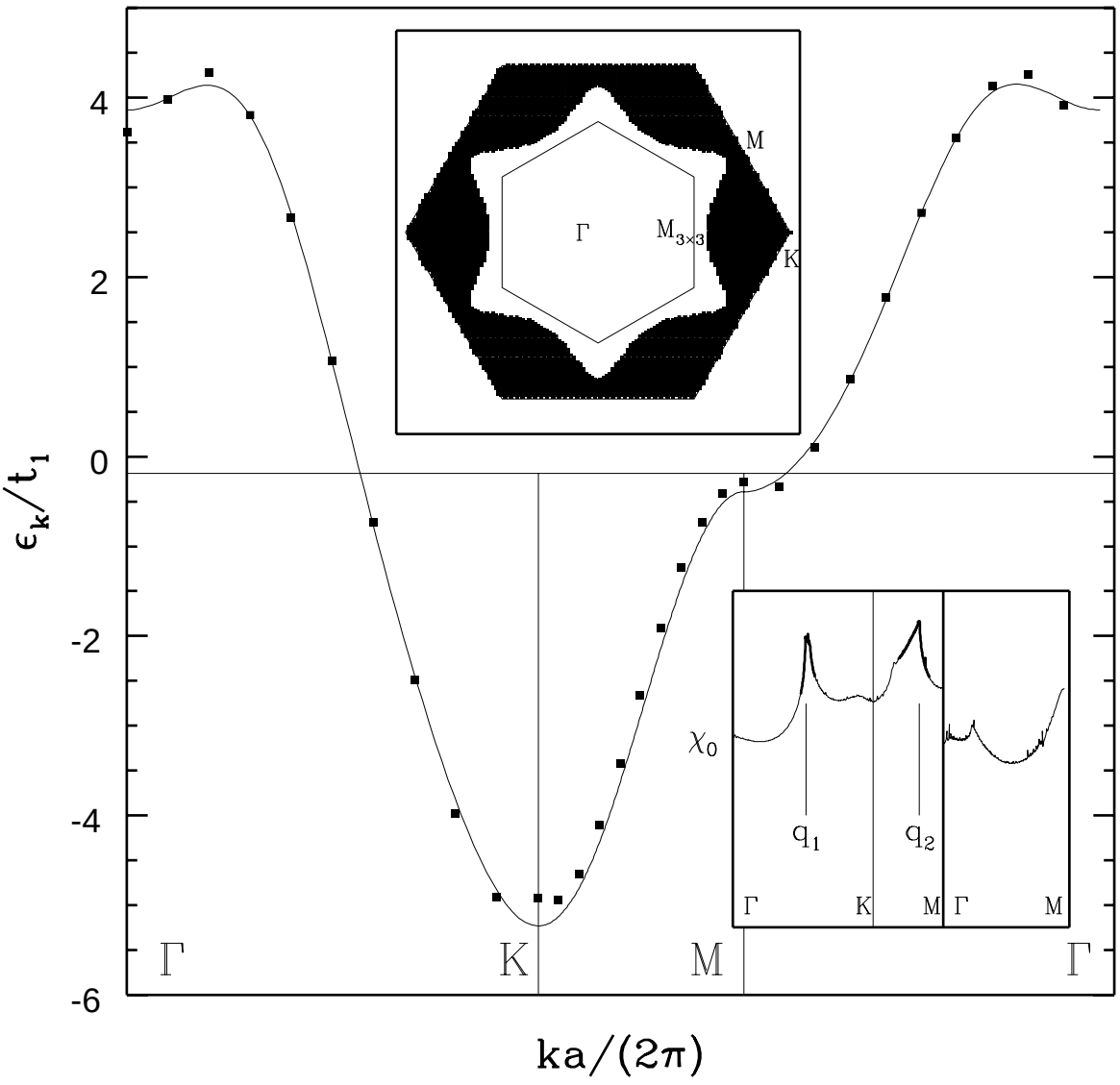
Figure Captions

Figure 1 Surface state dispersion for Si(111)/Si, as obtained from LDA (solid squares). The solid line is a tight-binding fit obtained by including up to the sixth shell of neighbors, $t_1, \cdots, t_6$. The fit gives $t_1 = 0.0551$ eV, and $t_2/t_1 = -0.3494$, $t_3/t_1 = 0.1335$, $t_4/t_1 = -0.0615$, $t_5/t_1 = 0.0042$, $t_6/t_1 = -0.0215$. Upper inset: The Fermi surface of the half-filled surface band. Notice the quite poor nesting at the BZ corner wavevector $\mathbf{K} = (4\pi/3a, 0)$. Lower inset: The zero temperature Lindhard function $\chi_o(\mathbf{q})$ for the half-filled surface band. Notice the two peaks located at $\mathbf{q}_1 \approx 0.525\mathbf{K}$ and $\mathbf{q}_2 \approx 1.32\mathbf{K}$, and no feature whatsoever at $\mathbf{K}$.

Figure 2 Schematic Hartree-Fock phase diagram of the $U - V$ model, at zero electron-phonon coupling, for the band structure shown in Fig. 1. Only the most important commensurate 3×3 phases have been studied.

Figure 3 Plot of the HF bands along high symmetry directions of the BZ for the s-SDW and two CDW $\phi_\rho = 0$ solutions: (a) at $U/t_1 = 9$ and $V/t_1 = 2$, the insulating s-SDW (ground state); (b) at $U/t_1 = 9$ and $V/t_1 = 2$, the insulating solution with a small CDW and $m^z = 1/3$ (meta-stable, the actual ground state being the s-SDW); Solid and dashed lines denote up and down bands, respectively. (c) at $U/t_1 = 4$ and $V/t_1 = 2$, the metallic solution with a large CDW and no magnetism.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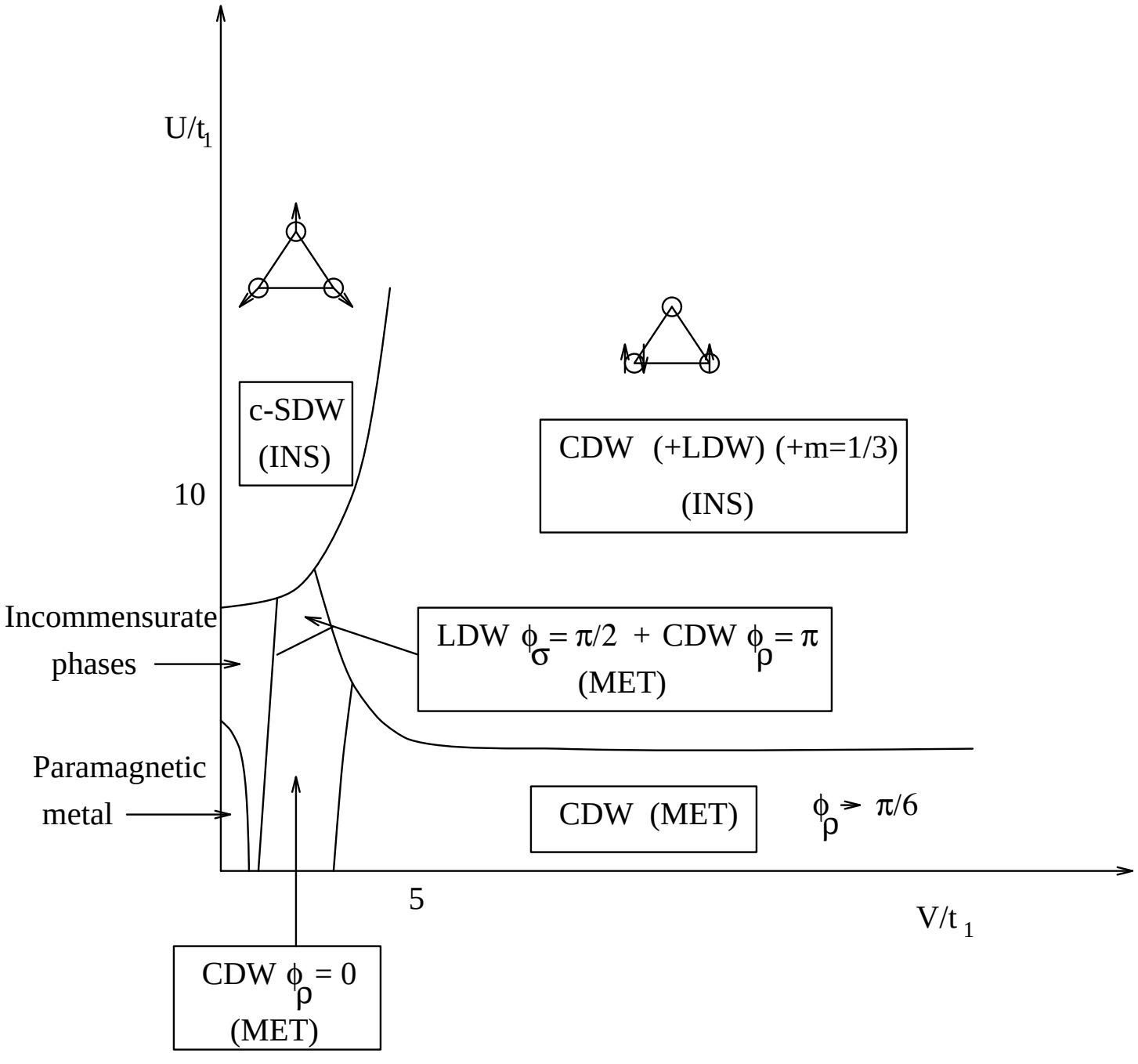
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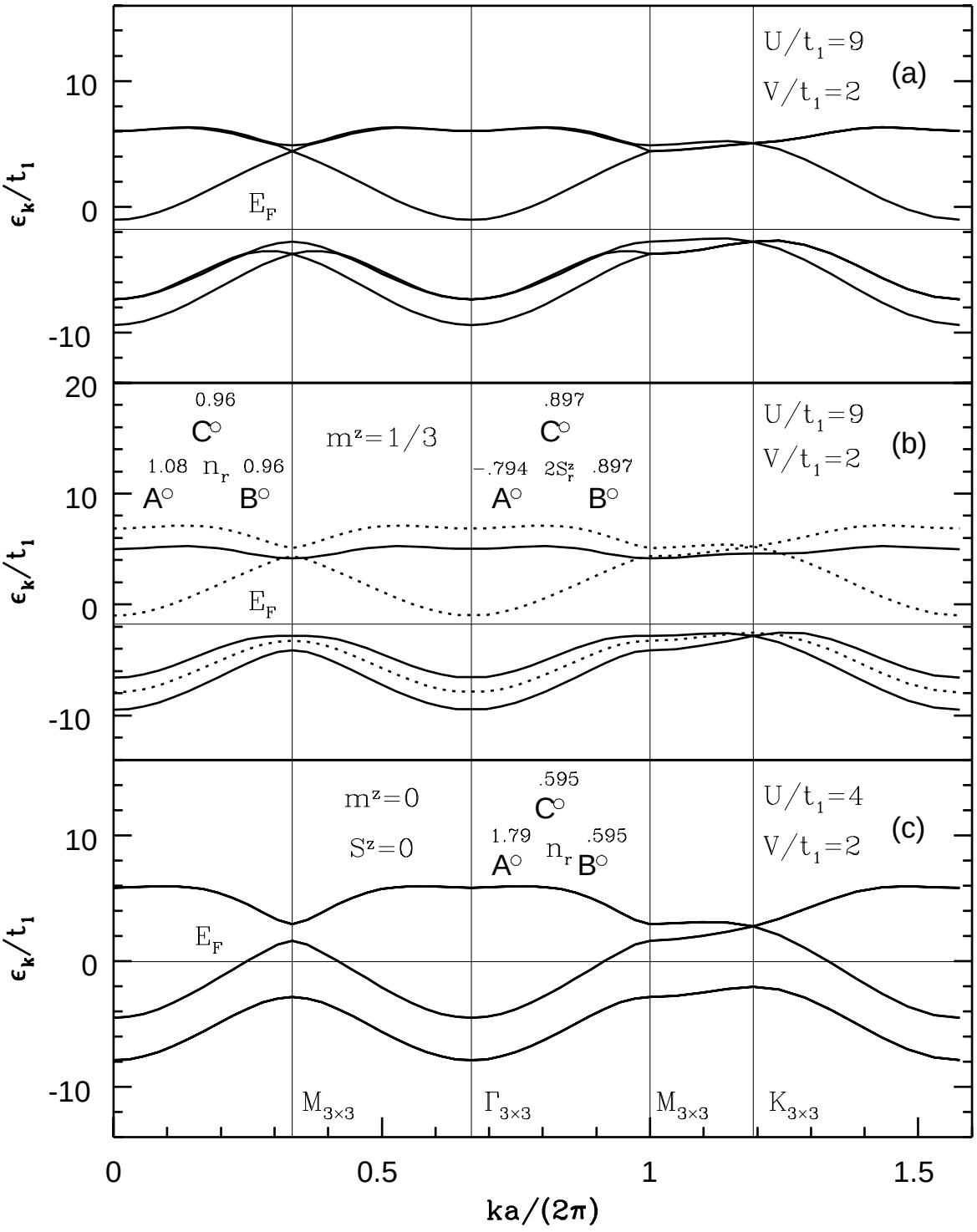
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